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Synthesis and Characterization of Antioxidant Resin Modified-Alkoxy from the Condensation of 4-HydroxyphenoxyPhenyl Propane (BisphenolA) with Formaldehyde

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Abstract
In this paper ,an antioxidant-modified resin were synthesized through the condensation of Bisphenol A with formaldehyde transferred to alkoxied .Antioxidant-modified and its alkoxy derivatives were synthesized .These kinds of alkoxy are useful in many fields such as antioxidants for lubricating oil. These functional hydroxyl groups after esterification were characterized by I.R.spectroscopy ,thermo gravimetric (TG),elementary analysis and NMR. The analytical results of I.R demonstrate the changes of hydroxyl groups and suggests that this synthesis was feasible .This study concern the effects of these additives on the autoxidation and degradation of lubricating oil properties such as viscosity, carbonyl index ,pour point and acid number. These alkoxy resins showed outstanding efficiency as antioxidant for lubricating oil relative to the commercial ones which reached in some concentrations about one eight folds of the commercial antioxidants.

1. Introduction

A lubricating oil may broadly defined as any substance that will reduced fraction between moving surfaces. Lubricating oils are usually used in the presence of air and catalysts, where by oxidative reactions can take place through the oxidation processes. Such oxidation have a drawback on oil ,thus leading to failures in lubricants that accompanied by damage of machines due to the formation of vicious ,solid bodies, or emulsions material which interfere with the regular distribution of lubricant(J.C.Jhonson,1975,J.Encina et al,2007,M.Resberger,1994).

The use of antioxidants become highly required to decrease oil oxidation and inhibit corrosion in certain part of the engine(B.D.Campbell,et al,1979).The antioxidant which act by targeting particular steps in the oxidation reactions. Generally antioxidant consider to be a free radical inhibitor of peroxide decomposition and may vary in chemical structures. Three types of additives have been proved to successful in controlling the degradation of lubricating oils, radical scavenger and hydro peroxide decomposers, as well as synergetic mixture of both of them. Thus various classes of compounds have been used as antioxidant additives such as phenols, amines and heterocyclic compounds(A.M.Omer,2001,P.Antony,et al,1996,M.M.Barboti,et al,1984),as well as synergistic mixtures of them and other additives(P..Antony,et al,2013,J.Zhu,et al,2013.In this work described the synthesis and evaluation of new type of Bisphenol A -formaldehyde resin and their alkoxy derivatives as antioxidants for lubricating oil.

2. Experimental

Synthesis and characterization:

The resin was synthesized in one pot reaction system by condensation of Bisphenol A with formaldehyde. The flanged top reaction vessel equipped with a five necked – lid bearing an efficient mechanical stirrer, thermometer, PH-meter electrode, condenser and separating funnel, immersed in a thermo stated water bath was charged with reactants i.e. phenol(0.2 mole), NaOH(0.2 mole),formaldehyde(37%)w/v(1mole).

The reaction was carried out at definite temperature ,time, PH and reactant mole concentration. The effect of all these factors was examined and the best conditions were found(N.A.Al-Jabiri,et al1995).After the reaction was completed ,the resinous layer was separated from the reaction mixture, purified by desalting procedure then dried and analyzed by elemental analysis(Resin I) and characterized by IR-spectroscopy(fig.1),the broad absorption band at 3300cm^{-1} is a characteristic . Band of hydrogen bonded methylol groups, which disappear in the ether derivatives(fig.2 , 3and 4 for resin II , III and IV)

The structure of resin(I) was found to be 2,4,6-tri methoxy phenol, the number of methylol groups was determined by the moisture evolution technique which was found to be three groups per unit which was confirmed by elemental analysis data :

(%Calculated %H=6.94,%C=65.5,%O=27.6)(%Found %H=7.11,%C=67.99,%O=28.1)

The calculation were based on the repeating unit structure.

The percentage of water found for resin(I) was 11.5% against the calculated value 10.34%.Resin (I) was transferred to the alkoxy derivatives as methoxy(II) ,(III)and(IV) with suitable alcohol followed by reflux for three hours and analyzed by elemental analysis :

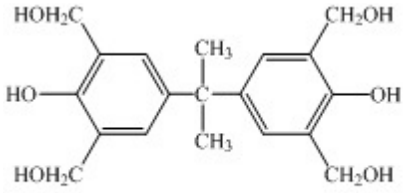
Resin(II) (%Calculated %H=8.62,%C=70.39,%O=21.28) (%Found %H=8.10,%C=67.99,%O=28.1)

Resin(III) (%Calculated %H=7.97,%C=68.27,%O=22.98) (%Found %H=7.12,%C=67.99,%O=28.1)
Resin(IV) (%Calculated %H=8.65,%C=72.62,%O=18.73) (%Found %H=9.00,%C=67.99,%O=28.1)
and characterized by IR(figs.2,3and 4) for resins II ,III and IV and ^{1}H-NMR(figs.5 and 6 for resin I and II .
The molecular weight of the resin and their alkoxy derivatives were determine by vapor pressure osmometer(Kanuer Vapour Pressure).Result shown in table(1)

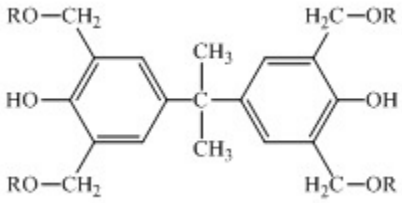
Table1. Molecular weight of reins I , II ,III and IV.

Resin	Molecular Weight Calculated	Molecular Weight Found
I	348	345±3
II	404	404±0
III	460	462±2
IV	512	512± 0

The expected structure of the methylolic and their alkoxy derivative are shown below:



2,2 { bis (3,5 dimethylol) 4- hydroxyl phenyl } Propane.



2,2 { bis (3,5 dialkoxy methylene) 4- hydroxyl phenyl } Propane.
Where : (II, R=CH_3) (III, R= CH_2CH_3) (IV, R=CH_2CH_2CH)
The number of hydroxyl groups and their ethers also determined by NMR, table(2) and figure (5) shows the chemical shifts of the resin I and their methoxy derivative resins II . The results obtained shows that all hydroxyl groups are etherized.

Table(2): ^{1}H NMR data for resins I , II .III and IV in CDCl3

Resin	Chemical shift (ppm)
I	1.9(S,3H,C-OH) , 3.5(S,6H,CH_2O) ,6.9-7.2(m,2H,Ar-H),9.8(S,1H,Ar-OH).
II	3.4(S,9H,CH_3) ,3.8(S,2H,CH_2O) ,4.8(S,4H,CH_2O) ,6.9-7,2(m,2H,Ar-OH) .
III	1.2(S,9H,CH_3) ,3.5(S,6H,CH_2O ,3.8(S,2H,CH_2O) ,4.5(S,4H,CH_2O),6.9(m,2H,ArH)
IV	0.5-1.7(S,15H,CH_2CH_3) ,3-5(S,6H,CH_2-C) ,6.9(m,2H,Ar-H), 7.8(S,H,Ar-OH).

3. Setting Characteristics of The Methyl Resin

3.1Thermogravimetric analysis
The thermosetting characteristics was used in studying the thermosetting behavior of the methylolic resin. The measurements were carried out by heating the resin at heating rate of 20°C/min. The rate of cross linking was followed as a function of weight loss due to the thermal treatment. Typical TG and DTG thermo grams are

shown in fig.(6) . The first loss peak due to the curing reaction i.e. dehydration and dehydroformulation reactions, weight percentage loss from(DTG) 20.3% for resin(I).

3.2Thermosetting study of the resin by moisture evolution analysis(MEA):

The MEA measurements were carried out on Du Pont Moisture Evolution Analyzer Model 930H.After calibration with standard materials, the measurements were carried out by heating samples from the resin at several different temperatures(100-170).The amount of water evolved from the crosslinking reaction was determined as a function of time and temperature. Result obtained are shown in fig.(7).

3.3Differential Scanning Calorimetry (DSC):

A Du Pont thermoanalyser Model1090 was used in the thermosetting investigation of the resin. The measurements were carried out by heating samples from the methylolic resin isothermally in the temperature range 80 – 120^{o}C.Typical DSC thermo grams are shown in fig.(9).Other samples from the resin were heated under dynamic condition at heating rate 2^{o}C/min.The curing characteristic of the isothermally set samples were studied by heating the samples at constant rate 20^{o}C/min and the DSC thermo grams obtained .

3.4Thermal stability of the resins:

The thermal stability of the resins was investigated by thermo gravimetric Analysis. The set resins shows outstanding thermal stability. The decomposition temperature as measured by DTG 397^{o}C as shown in figure (6).This is due to the low volatility and high temperature stability for these new resins. The formation of intermediate compounds such as quinols which responsible for thermal stability of these resins.

4. Thermal oxidation stability experiments:

The oxidation experiments of lubricating oil(SW40)carried out by standard method(I.P. 48/8,I.P.Method142/74) using different concentrations of resins. To accelerate the oxidation of lubricating oil iron naphthenate used at constant concentration(0.002%) with air flow rate 2.8cm³/sec. at 180°C at different intervals time.

The carbonyl number, acidity, pour point and viscosity of the lubricating oil were studied by using different concentrations of resins II, III and IV at interval times. Tables (3-11) shows these results .Figures (9,10 and 11) shows the formation of soluble acid with time for these resins.

5. Results and Discussion:

The new intermediate(resin I) and its alkoxy derivatives shows a good thermal stability and have an interesting properties as a high boiling point and low volatility.

The concentration of the antioxidants resin(II and III) does not exceed more than 1%.Table (3) shows the oxidation of lubricating oil without additives. After

15 minutes of oxidation, the physical properties of the oil changed completely,Since the oil stands without changed after 5 hours in the presence of resin II or III or IV.

5.1 Acidity

The acid number depends on the formation of carboxylic acids through the oxidation and this number increased with increasing the number of carboxylic groups. Tables (3-11) shows the results of the oxidation of lubricating oil in the presence of resin II,III and IV at different concentrations. The acidity number found to be 13.5 without antioxidant and this acidity reduced to 5.1 , 4.0 and 1.6 in the presence of resin(II) at concentration 0.2% , 0.3% and 0.5% respectively.Figures 10,11 and 12 shows the relationships between the soluble acid number with time for resins II,III and IV.

The pour point of lubricating oil does not changed in the presence of these resins through the oxidation process(tables 3-11).

5.2 Viscosity

The viscosity have studied through the oxidation with time. The results shown in table(3) indicate that viscosity of the lubricating oil changed from 13.2 centistokes before oxidation to 21.61 centistokes after oxidation without additives .Thus viscosity ratio and percentage changed in viscosity 1.36 and 63.34% respectively, since the viscosity changed slightly when resin(II) used(16.8,14.8 and 14.2) centistokes at concentrations 0.2% , 0.3% and 0.5% respectively as shown in tables(4-11).

5.3 Carbonyl Index

The reaction mechanism have followed through the oxidation procedure by measuring the carbonyl index at different time through the formation of carbonyl groups. The carbonyl index considers as one of the most important measurements to follow the changed in the physical and chemical properties of the lubricating oil. Figures(12, 13 and 14) shows the relationship between carbonyl index and oxidation time in hours the results indicates that carbonyl number decreased as the concentration of resin II,III and IV increased .

6. Conclution

(1)The oxidation stability of oil as measured by soluble acid number indicate that, the oxidation inhibitor efficiency follow the order:

Resin I I> Resin III > Resin IV and the concentration of the resin effect the degree of oil stability.
(2)The synthesized additives and their mixtures have a multifunction for pour point depressant ,improving viscosity and oxidation stability of oil .These results depend on activity of additives and their mixture at oil phase.

Table3. Oxidation Results Of Lubricating Oil(SW40) Without Additives(Resin I)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.0	0.1	13.23	-13
3	0.8	0.41	13.23	-13
6	3.9	0.53	=	=
9	10.2	0.79	=	=
12	13.5	1.3	21.6	=

Table4. Oxidation Results Of Lubricating Oil(SW40) with 0.2% Additives (Resin II)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.17	0.10	14.2	-16
3	0.14	1.53	=	=
6	0.40	1.61	=	=
9	1.17	2.55	=	=
12	5.1	3.60	14.82	-16

Table5. Oxidation Results Of Lubricating Oil(SW40) with 0.3% Additives

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.17	0.1	14.2	-16
3	0.13	1.35	=	-16
6	0.4	1.6	=	=
9	1.17	2.55	=	=
12	2.18	3.6	=	=

Table 6. Oxidation Results of Lubricating Oil(SW40) with 0.5% additives (Resin II)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.18	0.1	14.5	-16
3	0.10	1.27	=	=
6	0.14	2.85	=	=
9	0.40	4.07	=	=
12	4.0	0.1	14.9	-16

Table7. Oxidation Results of Lubricating Oil(SW40) With 0.2% Additives (Resin III)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.25	0.30	13.1	-16
3	0.90	0.42	=	=
6	2.2	-	=	=
9	4.1	1.34	=	=
12	1.6	1.50	14.2	-13

Table 8. Oxidation Results Of Lubricating Oil(SW40) With 0.3% Additives (Resin III)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.25	0.30	12.9	-16
3	0.44	1.30	=	=
6	1.10	5.18	=	=
9	2.95	10.40	=	=
12	4.0	11.78	14.90	-13

Table 9. Oxidation Results Of Lubricating Oil(SW40) with 0.5% additives(Resin III)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.12	0.20	14.28	-16
3	0.22	3.10	=	=
6	0.37	3.60	=	=
9	0.6	9.30	=	=
12	0.86	10.20	14.28	=

Table 10. Oxidation Results Of Lubricating Oil(SW40) with 0.2% additives (Resin IV)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.10	0.20	12.8	-16
3	0.18	2.20	=	=
6	0.28	3.29	=	=
9	0.89	7.41	=	=
12	1.75	3.29	16.4	-13

Table 11. Oxidation Results Of lubricating Oil(SW40)with 0.3% Additives (Resin IV)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.15	0.20	13.0	-16
3	0.16	3.10	=	=
6	0.2	4.10	=	=
9	0.64	10.40	=	=
12	0.96	11.80	15.2	=

Table12. Oxidation Results of lubricating oil(SW40)with0.5% Additives(Resin IV)

Time	No.(SA)	Carbonyl Index	Viscosity	Pour point
Zero	0.14	0.3	13.1	-16
3	0.2	0.44	=	=
6	0.2	3.14	=	=
9	0.3	5.56	=	-16
12	0.45	8.2	14.1	-16

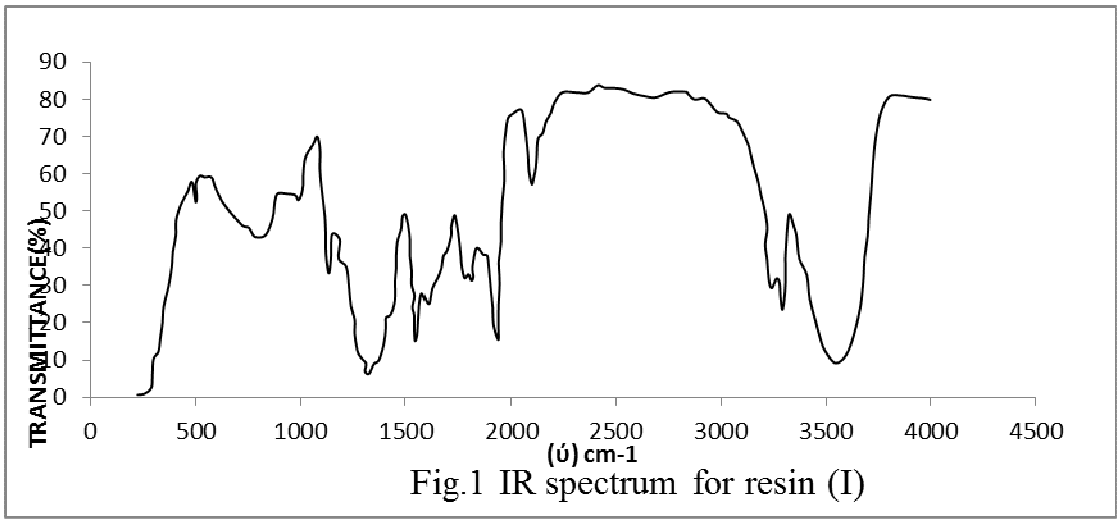


Fig.1 IR spectrum for resin (I)

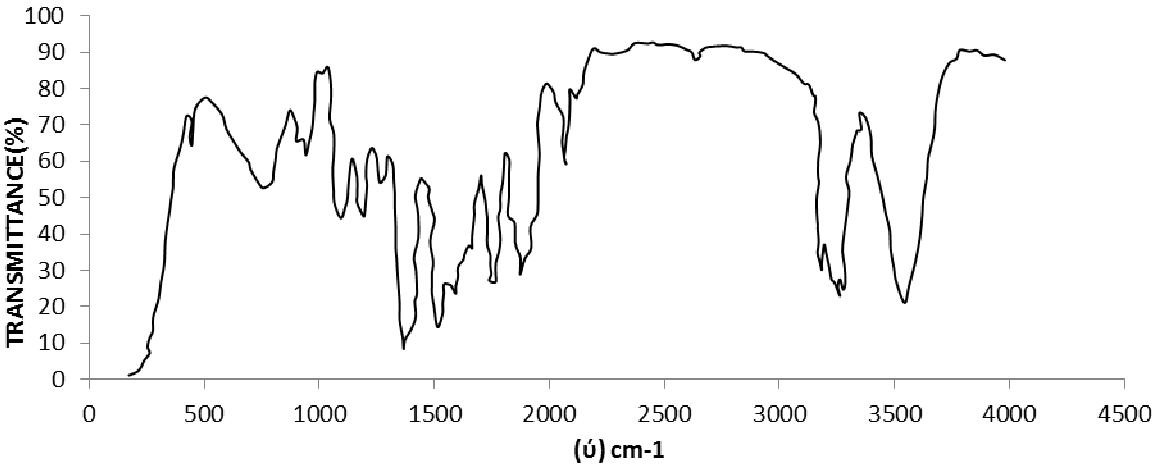


Fig.2 IR spectrum for resin (II)

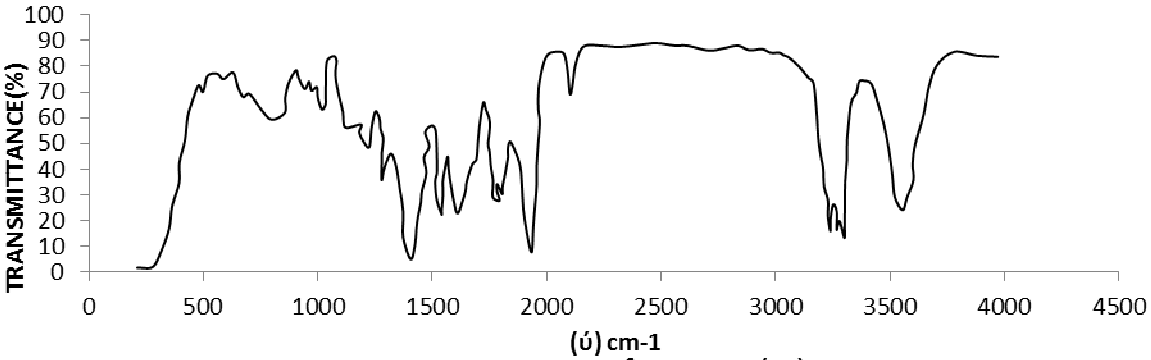


Fig.3 IR spectrum for resin (III)

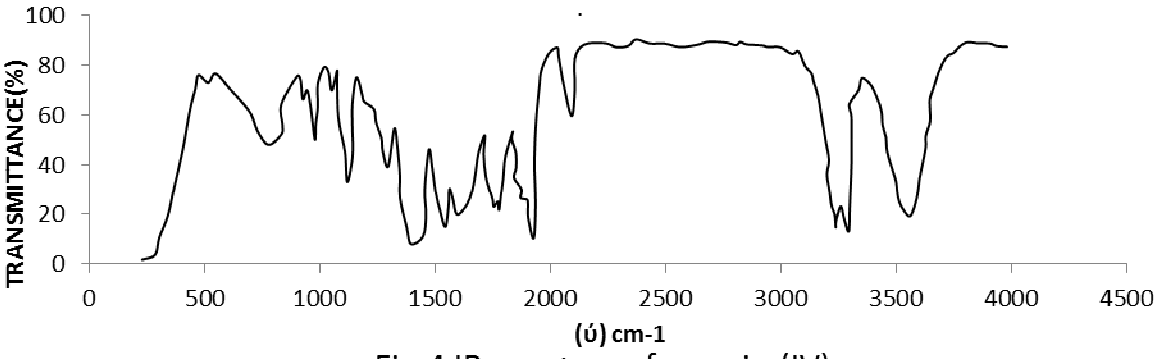


Fig.4 IR spectrum for resin (IV)

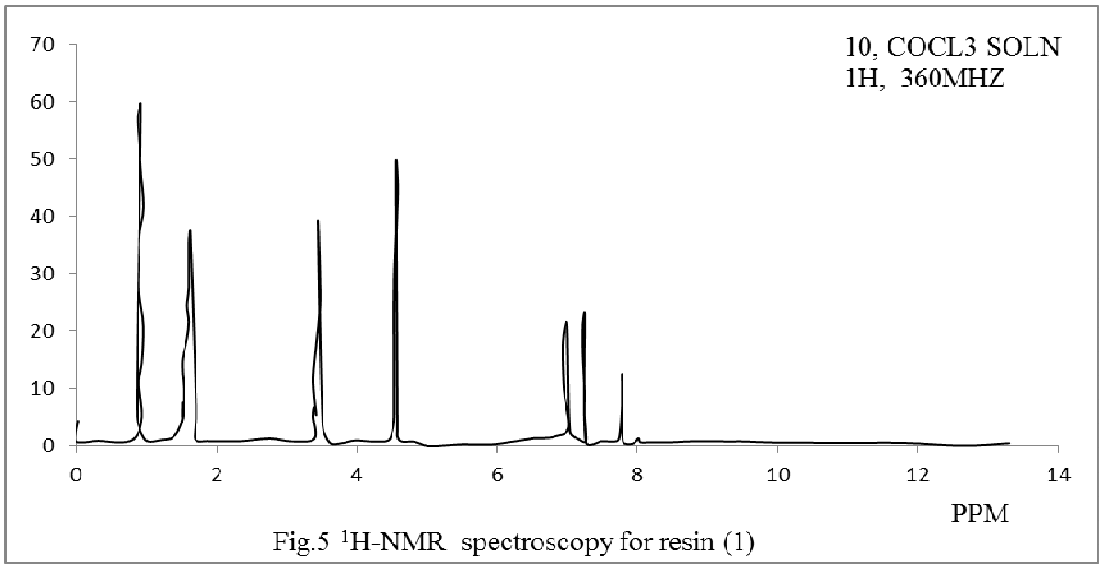


Fig.5 ^{1}H-NMR spectroscopy for resin (1)

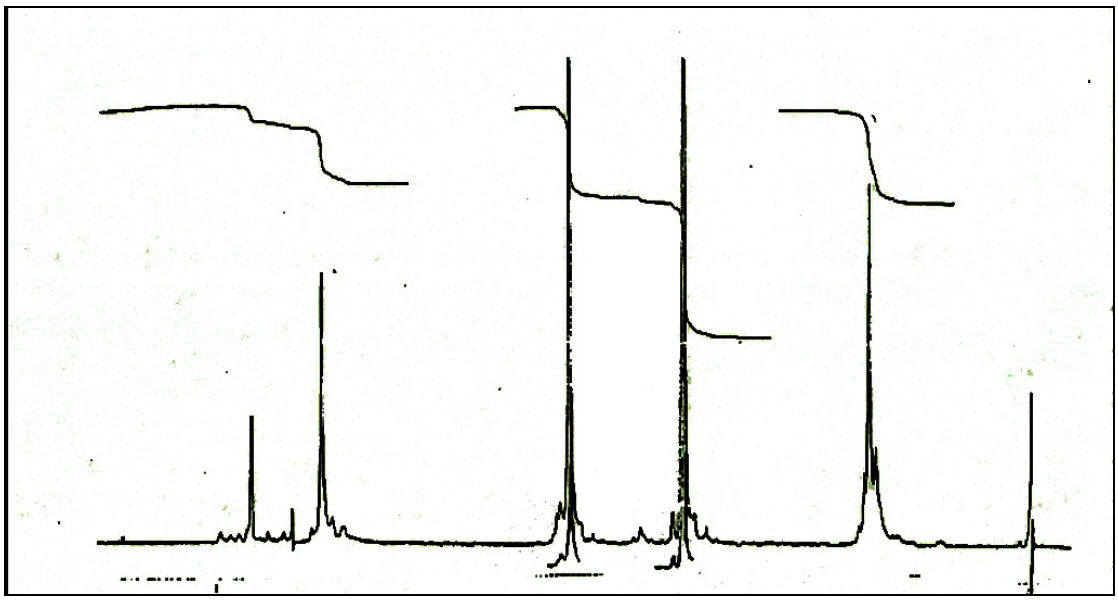


Fig.6 : ^{1}H – NMR spectroscopy for resin (II)

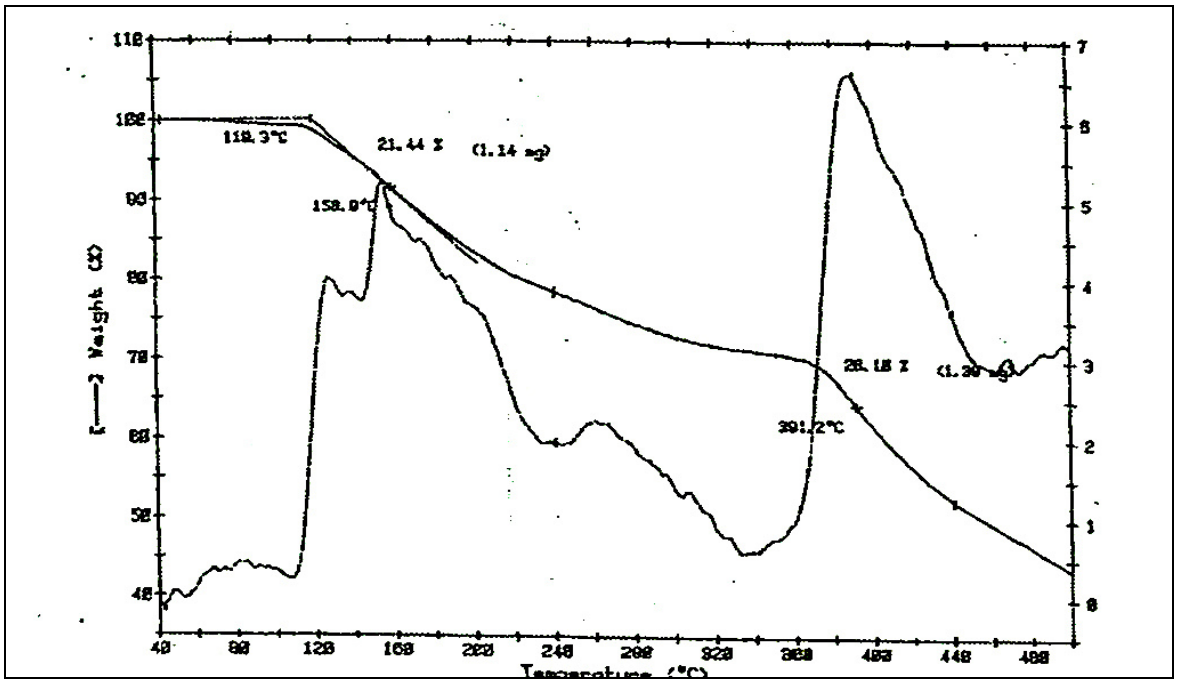


Fig.6: Typical thermogravimetric of resin (I) measured at 20°C/min

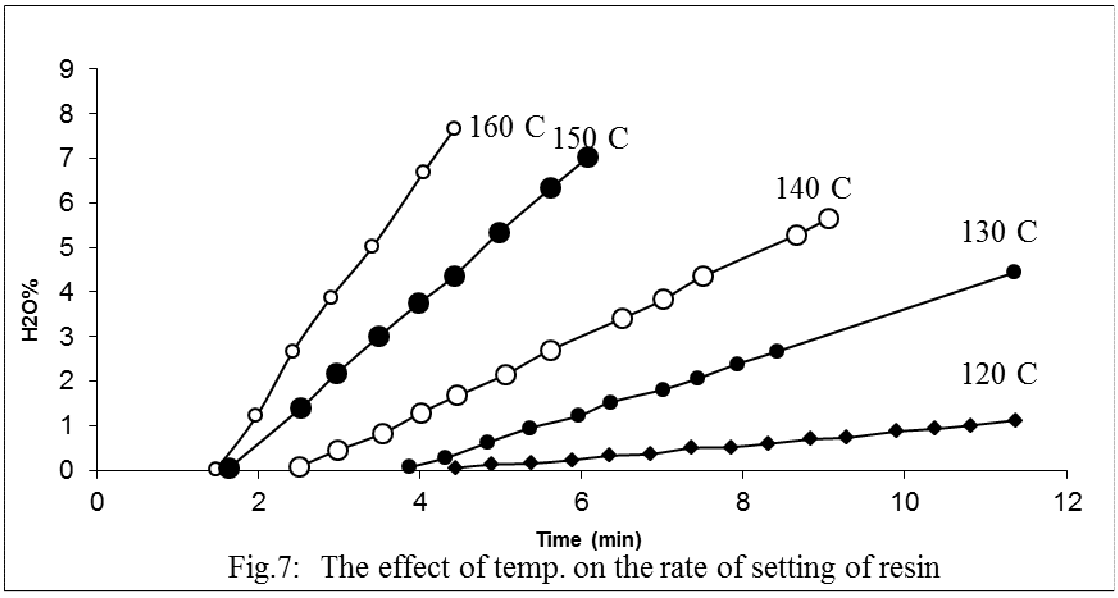


Fig.7: The effect of temp. on the rate of setting of resin

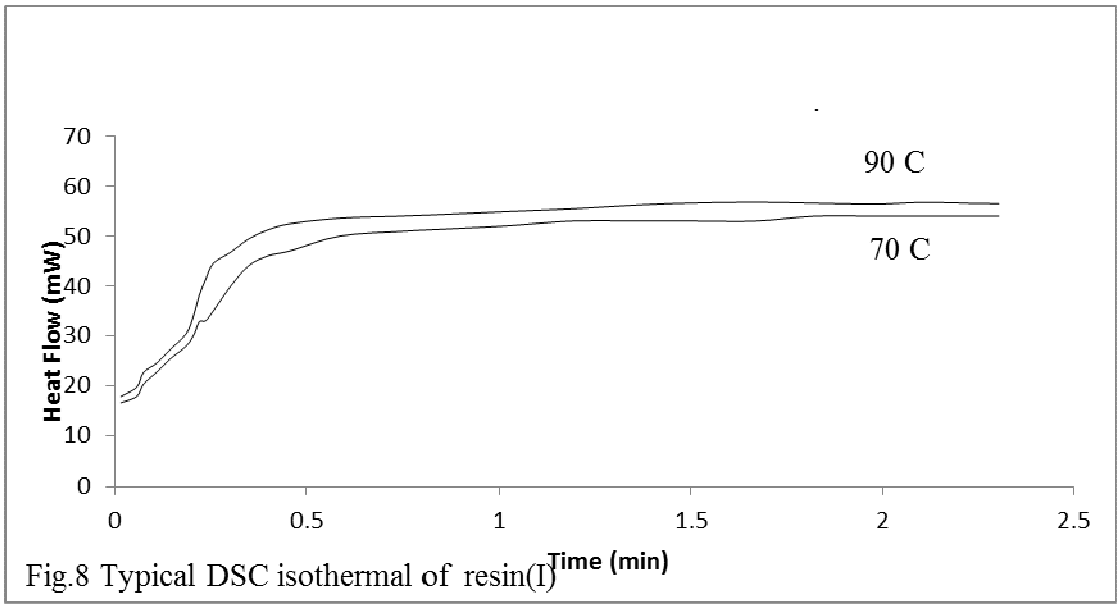


Fig.8 Typical DSC isothermal of resin(I)

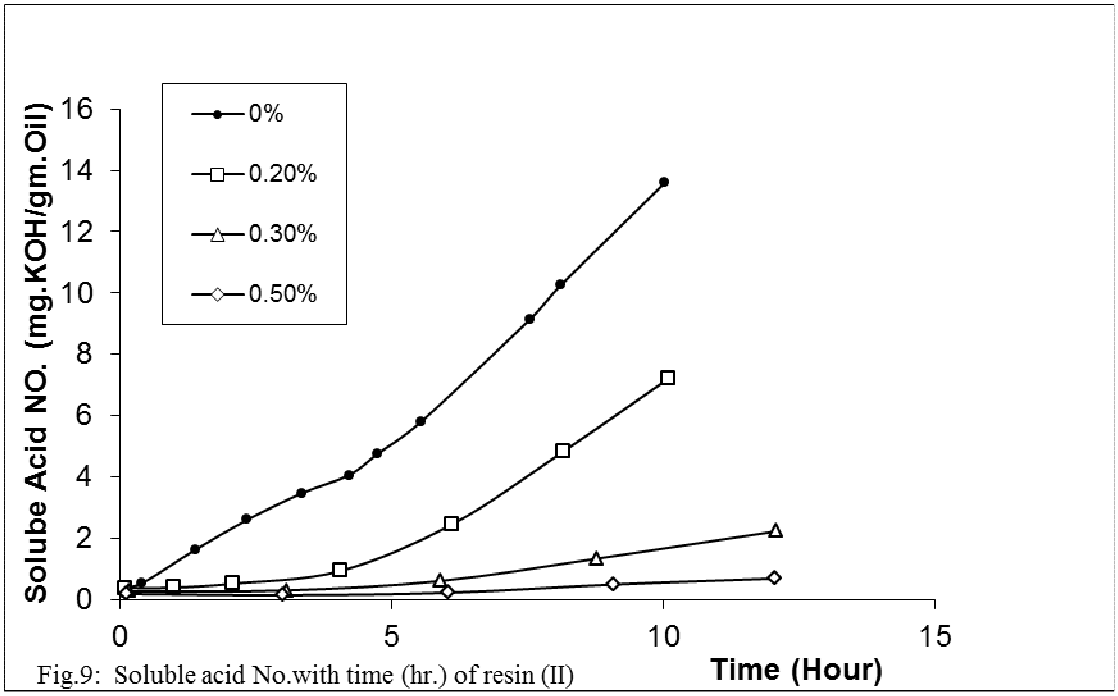


Fig.9: Soluble acid No.with time (hr.) of resin (II)

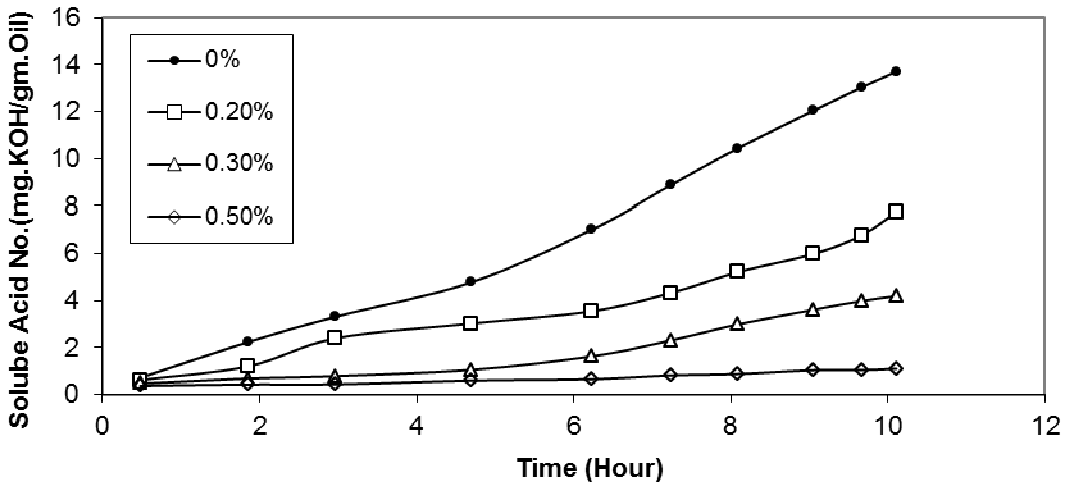


Fig.10:Soluble acid No. with time(hr.) of resin (III)

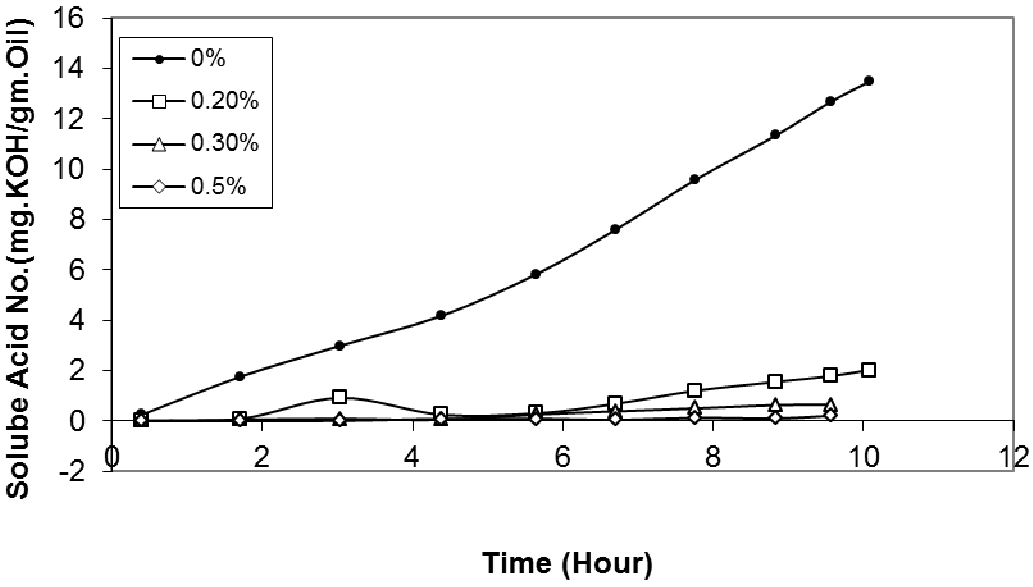


Fig.11:Soluble acid No. with time(hr.) of resin (IV)

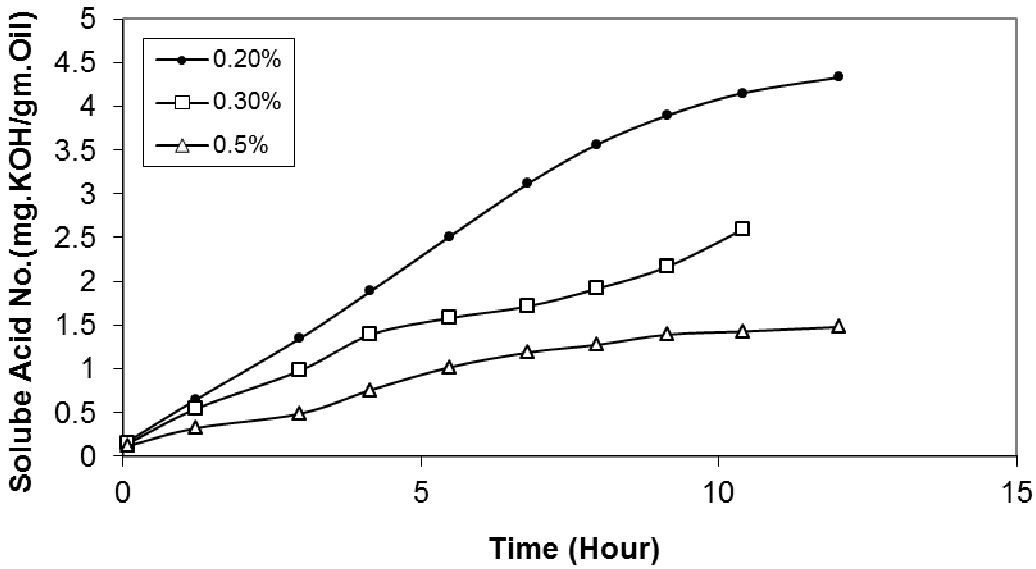


Fig.12: Carboyl index with time(hr.) of resin (II)

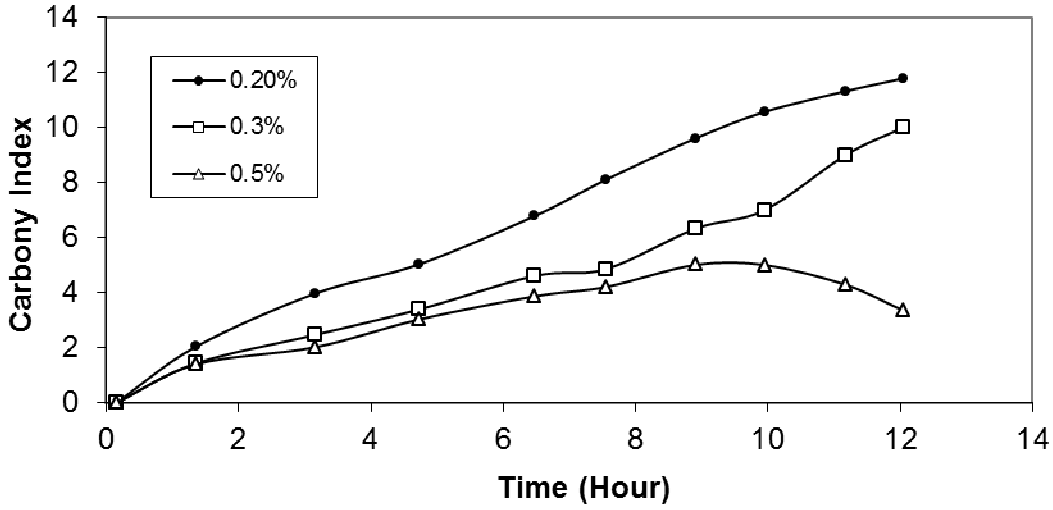


Fig.13: Carboyl index with time(hr.) of

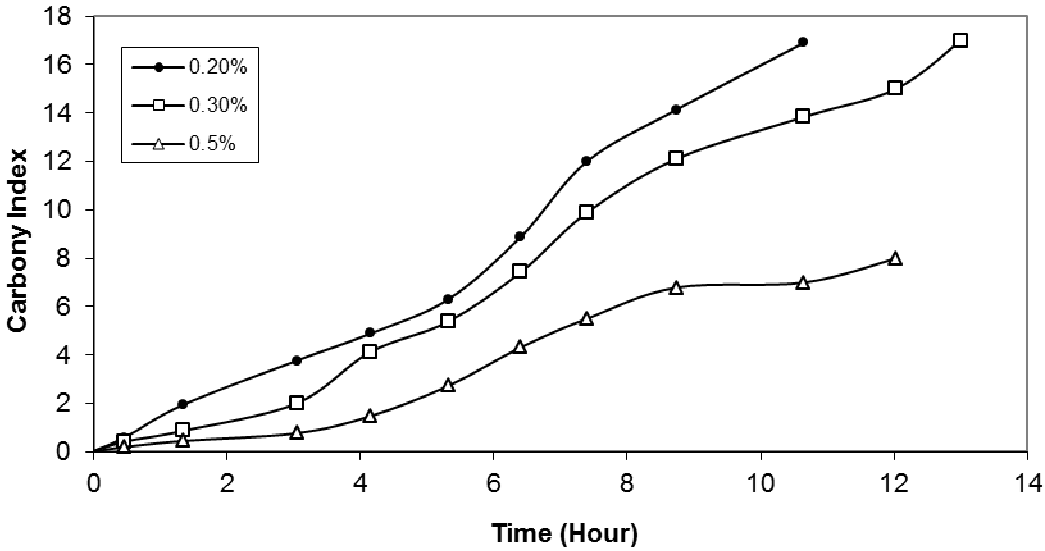


Fig.14: Carboyl index with time(hr.) of resin (IV)

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